

CHEMICAL MODIFICATION OF FAST-GROWN POPLAR BY UREA FORMALDEHYDE AND POLYACRYLIC RESIN

Zeng Bi

Postgraduate Student
E-mail: bizeng@yeah.net

Qian Lang

Postgraduate Student
E-mail: langqian4521@126.com

*Junwen Pu**

Professor
School of Material Science and Technology
Beijing Forestry University
Haidian, China 100083
E-mail: bjfu4521@126.com

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Abstract. In this study, methylolurea and polyacrylic resin were used to modify fast-grown poplar. The dimensional stability and mechanical properties of natural and modified wood were investigated. Also, the modified samples were characterized by scanning electron microscopy, X-ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR), and thermogravimetric analysis (TGA). The results showed that the chemical modifier was impregnated into the wood inner structure, which improved the chemical and mechanical performance of wood. FTIR demonstrated that the hydroxyl groups of wood were decreased, which decreased the water absorption of natural wood. XRD tests indicated that the crystallinity of wood increased but the structure of cellulose was not disrupted after modification. TGA analysis showed that the thermal stability of the hemicelluloses and cellulose was enhanced after modification. The prepolymer was not only impregnated into the wood cell, but also reacted with the wood fiber. A crosslinking reaction occurred between the wood modifier and wood fiber.

Keywords: Chemical modification, methylolurea and polyacrylic resin, fast-growing poplar, impregnation.

INTRODUCTION

As an important renewable resource, wood is widely used in industries such as construction, transportation, spaceflight, etc. With the rapid development of the wood industry, high-quality wood materials are urgently demanded. Consequently, fast-grown wood is widely grown around the world, especially in China. However, fast-grown wood shows a number of insufficient characteristics, such as low density, poor dimensional stability, and poor mechanical properties (Chen et al 2013). Therefore, improving the properties of fast-grown wood is essential. Wood modification is a promising way of improving

wood properties. Furthermore, wood modification has become an important method to help manufacturers tailor competitive wood products to a wider range of applications (Hansmann et al 2005).

In recent years, many efforts and studies have been undertaken to improve wood properties (Unger et al 2013). Wood modification can be defined as an application with chemical, physical, mechanical, and biological methods to improve the inner or surface structure of wood. Wood can be modified in many ways. Chemical modification using small organic molecules is one of the most important methods. A variety of wood properties can be changed through chemical modification, including improvements in dimensional stability, biological durability, surface hardness

* Corresponding author

and wear, hydrophobic nature, fire retardancy, and color (Hansmann et al 2005). Meanwhile, chemical modification has been recognized as an important alternative to preservatives in the wood protection industry (Xie et al 2013).

The possible methods of chemical modification have been described in many studies. Chemicals include methyl polymethacrylate, tetraethoxysilane, methyltriethoxysilane, glutaraldehyde, vinyl acetate, acetic anhydride, furfuryl alcohol, and 1,3-dimethylol-4,5-dihydroxyethyleneurea (Homan and Jorissen 2004; Dieste et al 2008; Mamiński et al 2013). Thermal treatment is also an effective method for wood modification. High temperature in wood causes degradation of the hemicelluloses and the amorphous region of cellulose, thereby contributing to the increase in the degree of crystallinity of this polymer. In addition, crosslinking between lignin and polymers occurs because of the thermal degradation of the wood, which is responsible for the decrease in hygroscopicity and improvement of dimensional stability (Severo et al 2012).

The study of wood chemical modification has increased in recent years. Devi and Maji (2012) investigated chemical modification of Simul wood by impregnation with styrene-acrylonitrile copolymer, glycidyl methacrylate (GMA), and organically modified nanoclay. The physical properties of wood polymer composites were improved because of the addition of GMA and nanoclay. Fabiyi et al (2011) investigated the surface properties of fast-grown poplar by impregnation with methacrylate polymer. Density and hardness were increased. The modified wood also showed good abrasion resistance compared with natural wood. Unger et al (2013) investigated the wood chemical modification by sol-gel-derived silica. The dimensional stability and other properties were enhanced. Cavallaro et al (2013) indicated that wood thermal stability was improved after chemical modification.

Wood is a porous material consisting of various cell structures composed primarily of biopolymers (carbohydrate polymers of cellulose and hemicelluloses and phenolic polymers of lignin)

and minor amounts (5-10%) of extractives (Devi and Maji 2012). Chemical modification can generally be classified as either cell wall modification or filling of large cell cavities or a combination of both. Cell wall modification refers to the process whereby wood cell wall constituents are altered through reacting with low-molecular-weight monomers or oligomers or by heating under high-temperature conditions. Filling of cell cavities is the process by which chemicals are deposited in the large cell cavities, such as lumens and vessels, and block the physical passages, thereby decreasing water-moisture access to wood cell walls (Hill 2007; Del Menezzi et al 2009). A number of hydroxyls exists in the cell wall structure of wood, which are mainly hydrophilic and active groups in the components of wood. An effective blockage of the wood components can prevent sorption of water in the cell walls as well as establish a high and stable degree of mineralization (Unger et al 2013).

Fast-growing wood has been planted around the world. In this study, large panel poplar was impregnated with polyacrylic resin. There was no need to dry the wood before impregnation. Also, chemical modification and the drying process were used together to modify the fast-grown wood, which enhanced the efficiency of wood modification. To investigate the properties of modified fast-growing wood, the urea-formaldehyde prepolymer and polyacrylic resin were used to modify the natural fast-growing wood by vacuum-pressure impregnation. After drying treatment, the modified woods were characterized in terms of mechanical properties, reactivity of functional groups, crystallinity, thermal stability, and their microstructure.

MATERIALS AND METHODS

Materials

Fresh poplar (*P. × euramericana* “108”) wood was obtained from Hebei province, China. Diameters of the 4- to 6-yr-old trees were 15-20 cm, and initial moisture contents of the fresh wood ranged from 70 to 80% before impregnation.

The mean basic density of the specimen was $390 (\pm 4.8\%) \text{ kg/m}^3$.

$$\rho_y = \frac{M_0}{V_{\text{MAX}}}$$

where ρ_y is specimen basic density, M_0 is mass of oven-dry specimen, and V_{MAX} is volume of the saturated water specimen.

Preparation of Prepolymer

A three-necked flask was charged with formaldehyde, urea, and ammonia at the molar ratio of 1.3:1.0:0.04 (Pu et al 2009a). The reaction mixture was heated to 40°C for 3 h with mechanical stirring. Sodium hydroxide and hydrochloric acid were used to adjust the pH of the prepolymer within the range of 5-7. Ten percent (w/w) $\text{K}_2\text{S}_2\text{O}_8$ was added as a stabilizing agent, and 5% (w/w) polyacrylic resin was added to the prepolymer solution. The mixture prepolymer was prepared for impregnation.

Impregnation and Kiln-drying

The dimensions of the wood samples for impregnation were $1000 \times 100 \times 25 \text{ mm}$ (length \times width \times thickness). The poplar samples were put into a vacuum-pressure vessel. After vacuumizing, 15% carbamide (w/w) and 15% prepolymer (w/w) were added to the vessel. Hydraulic pressure was gradually increased from 0.5 to 2.5 MPa. Hydraulic pressure was maintained for 2 h at 2.5 MPa. After impregnation, the wood samples were put into a kiln for drying. To prevent deformation, 0.2-MPa mechanical pressure was applied to the wood. Drying took approximately 130-150 h (Pu et al 2009b).

Density and Dimensional Stability

Density, water absorption, and swelling of natural and modified wood were tested according to Chinese standard GB/T 1934-2009 (Chinese standard 2009a, 2009b, 2009c). Wood sample dimensions were all $20 \times 20 \times 20 \text{ mm}$ (longitudinal [L] \times tangential [T] \times radial [R]) for the

three tests. Samples for the test of water absorption were completely immersed in water at $20 \pm 2^\circ\text{C}$ for 96 h. Then water uptake was calculated based on weight percentage gains after 6, 24, 48, 72, and 96 h with removal of excess water on the surface. Samples for the test of swelling rate were put in a humidity chamber at $20 \pm 2^\circ\text{C}$ and $60 \pm 3\% \text{ RH}$. Thickness swelling rates were calculated based on the midspan thickness changes after 6-h intervals. At least 10 samples were measured for each test.

Mechanical Properties

Natural and modified wood samples were analyzed with a universal mechanical testing machine (AG 100KNIMO, Tokyo, Japan). Tests were carried out according to Chinese standards (Chinese standard 2009d, 2009e, 2009f, 2009g). Wood samples were sawn into corresponding dimensions for different tests. The dimensions were $300 \times 20 \times 20 \text{ mm}$ (L \times T \times R) for the tests of bending strength and modulus of elasticity (MOE). The method was a three-point flexure test at a press rate of 1 mm/min. The dimensions were $30 \times 20 \times 20 \text{ mm}$ (L \times T \times R) for the test of parallel-to-grain compressive strength. Dimensions for the test of hardness were $70 \times 50 \times 50 \text{ mm}$ (L \times T \times R). At least five samples were measured for each test.

Scanning Electron Microscopy Analysis

A JOEL model JSM model scanning electron microscope (SEM) (Tokyo, Japan) was used to observe both the natural and modified samples. Wood samples were immersed in liquid nitrogen for 10 min. Then the samples were taken out and sliced to 50-70 μm by a slicing machine. After freeze-drying, samples to be observed under the SEM were mounted on conductive adhesive tape, sputtercoated with gold, and observed in the SEM with a voltage of 15 kV.

X-ray Diffraction Analysis

The natural and modified wood specimens were ground into wood powder. The wood powder

Table 1. Density and dimensional stability of natural and modified wood.

Name	Air-dried density (g/cm ³)	Oven-dried density (g/cm ³)	Basic density (g/cm ³)	Water absorption (%)	Swelling of transection (%)	Swelling of radial (%)	Swelling of longitudinal section (%)
Natural wood	0.44 (±0.018)	0.41 (±0.017)	0.39 (±0.019)	121.3 (±18.6)	3.8 (±0.18)	4.6 (±0.20)	0.52 (±0.015)
Modified wood	0.69 (±0.013)	0.64 (±0.011)	0.51 (±0.010)	78.5 (±9.3)	2.9 (±0.11)	3.4 (±0.11)	0.43 (±0.013)

was filtered with a 40-mesh sieve. The crystallinities of the samples were evaluated using a Shimadzu diffractometer (Model XRD 6000; Tokyo, Japan). The measurement conditions were CuK α radiation with graphite monochromator, 30-kV voltages, and 40-mA electric current. The patterns were obtained within a 10 to 50°2 θ angular interval with a 0.05° step and a scan rate of 2°·min⁻¹. The degree of crystallinity was calculated based on the ratio of the intensity differences in the peak positions by the X-ray diffraction (XRD) analyzer.

Fourier Transform IR Spectroscopy Analysis

The natural and modified wood powder specimens of 120-mesh size were tested with a Tensor 27 (Bruker, Germany) spectrometer. The dried specimens were embedded in potassium bromide pellets. They were recorded in the absorption mode in the range of 4000-400 cm⁻¹ with an accumulation of 64 scans at a resolution of 4 cm⁻¹.

Thermogravimetric Analyzer Analysis

The thermogravimetric behavior of natural and modified wood powder samples of 120 mesh size were characterized by a thermogravimetric analyzer (TGA) (Shimadzu DTG-60, Tokyo, Japan). The sample pan was placed on the Pt basket in the furnace and then heated from room

temperature to 600°C. The heating rate was 10°C·min⁻¹. α -Al₂O₃ was taken as the reference material. During testing, the heating unit was flushed under a continuous nitrogen flow at a pressure of 8-10 kPa.

RESULTS AND DISCUSSION

Density and Dimensional Stability

Table 1 shows the density and dimensional stability of natural and modified wood. The density of modified wood was higher than that of natural wood. The air-dried density, oven-dried density, and basic density increased by 56.82, 56.09, and 30.77%, respectively. The water absorption and swelling of fast-growing wood was obviously improved. The water absorption decreased from 121.3% (natural wood) to 78.5% (modified wood), which might have been caused by the chemical reaction between the prepolymer and the hydroxyl groups in wood. Since hydroxyl groups are the main hygroscopic groups in wood, less hydroxyl groups leads to lower water absorption and swelling (Islam et al 2012).

Mechanical Properties

Table 2 shows the mechanical properties of natural and modified wood. After modification, the modified wood exhibited improvement in bending strength, MOE in static bending, and parallel-to-grain compressive strength compared

Table 2. Mechanical properties of natural and modified wood.

Name	Bending strength (MPa)	Modulus of elasticity in static bending (MPa)	Parallel-to-grain compressive strength (MPa)	End hardness (N)	Tangential hardness (N)	Radial hardness (N)
Natural wood	83.3 (±6.7)	7,655 (±821)	47.1 (±7.1)	3497 (±337)	1493 (±171)	1402 (±159)
Modified wood	122.8 (±5.8)	11,976 (±696)	68.2 (±5.7)	4667 (±214)	2824 (±128)	2876 (±136)

with the natural samples. The average values of modified wood samples increased by 47.42, 56.45, and 44.80%, respectively. Hardness of modified wood also improved compared with the natural wood samples. Increases were 33.46, 89.15, and 105.14% on end hardness, tangential hardness, and radial hardness, respectively. These results could be explained by the fact that the wood cell wall and cell cavity were filled with the prepolymer and polyacrylic resin, which increased the wood density (Heräjärvi 2009). The improvement of physical and mechanical properties was caused by the increase of density and the reaction between the prepolymer and wood cell. The crosslinking reaction occurred between the prepolymer and prepolymer, and prepolymer, and wood fiber. These reactions formed a mesh structure to fill the wood catheter and intercellular spaces. This mesh structure

made an efficient connection between the wood cells. Wood internal structure became more compact. Therefore, the wood properties were improved significantly.

Scanning Electron Microscope Analysis

To observe the fracture surface morphologies, the natural and modified wood samples were tested by SEM. The natural wood samples (Fig 1a) exhibited a highly void structure. However, after impregnation, for the modified wood samples (Fig 1b), the wood modifier obviously existed in the empty spaces. The empty spaces marked by the white line that got significantly smaller. The chemicals can be homogeneously dispersed in the cell wall and other vertical cells after vacuum-pressure impregnation. Furthermore, the radial sections of natural and modified wood

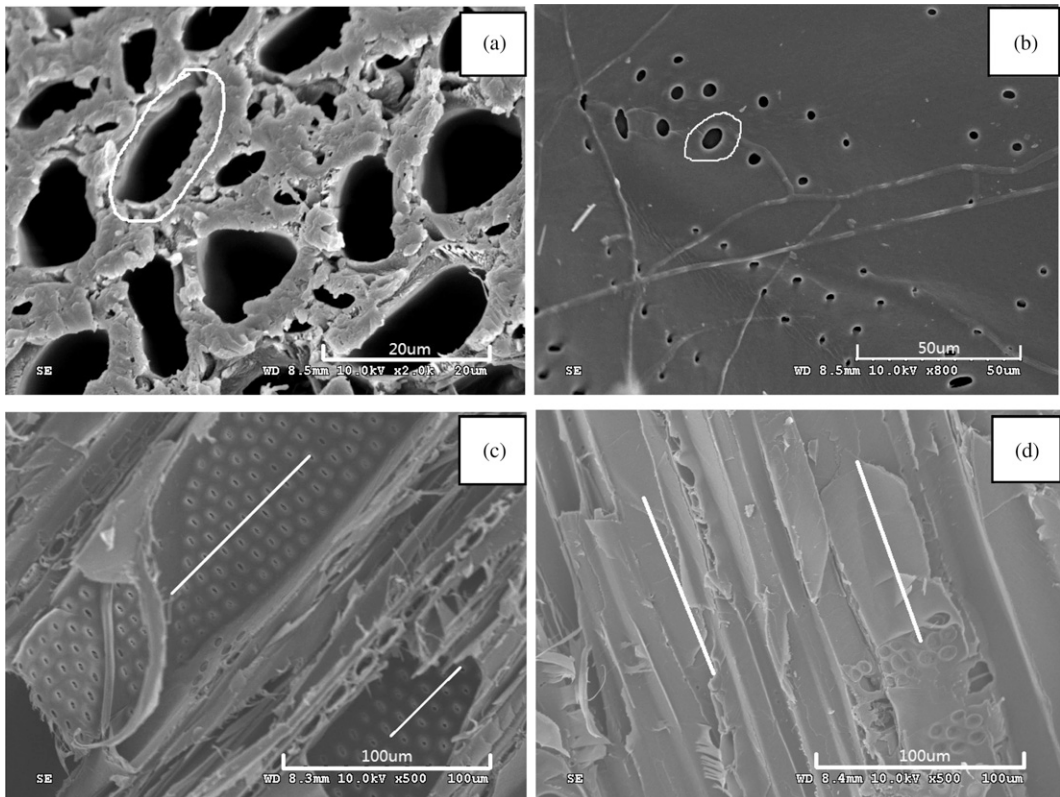


Figure 1. Scanning electron micrographs of natural and modified wood: (a) transection of natural wood, (b) transection of modified wood, (c) radial section of natural wood, (d) radial section of modified wood.

are shown in Figs 1c and 1d, respectively. It shows clearly that the natural wood surfaces were covered by a rough interface and empty spaces marked by the white line, which showed a number of void and pore spaces. However, the surfaces of treated wood were smooth. It was also clearly visible that the chemical particles were distributed as rod-like or discontinuous in the wood cells. The SEM studies provided evidence that the wood modifier had good dispersion in the cell wall and intercellular spaces. It meant an interface bonding existed between the wood fiber and wood modifier.

X-ray Diffraction Analysis

XRD spectra of natural and modified samples are shown in Fig 2. It presents the patterns of wood crystalline phases. Commonly, for natural wood, the diffraction angle peaks at 16.5° , 22.5° , and 35.0° corresponded to the cellulose crystallographic planes I_{101} , I_{002} , and I_{040} , respectively (Mulinari et al 2010). The peak positions of modified wood were almost unchanged, which meant that the structure of cellulose was not disrupted after modification. Also, after impregnation, wood crystallinity increased from 39.62 to 41.66%. The change in crystallinity of modified wood shows that the wood modifier filled in the microfibril of the cell wall. A crosslinking reaction occurred between the prepolymer and

wood fiber, which may have led to rearranging of the cellulose molecule chains and formed a part of the crystalline region (Lang et al 2013).

Thermogravimetric Analysis

TGA curves of natural and modified wood are presented in Fig 3. It is shown that there were obviously four stages of thermal degradation during the test. The loss of wood mass at 170°C was about 2% in the first stage, which can be concluded as the loss of volatile components, such as free water, from wood powder (Joshi et al 2005). For the second stage, a rapid mass loss of 32% in wood powder was recorded in the temperature range of $170\text{--}330^\circ\text{C}$. This was caused by degradation of wood and prepolymer during the heat treatment process and decomposition of hemicellulose. However, thermal degradation of natural wood was faster than that of modified wood. The difference can be attributed to the crosslinking reaction that occurred between the prepolymer and wood fiber, which enhanced the thermal stability of wood. For the third stage, a rapid mass loss of 63% in wood was recorded. This was because of oxidative decomposition of the cellulose in the wood. In the last stage, mass loss of residual materials of wood powder was found to be slow at $410\text{--}600^\circ\text{C}$ (Tsiopstias and Panayiotou 2011). This was because of the

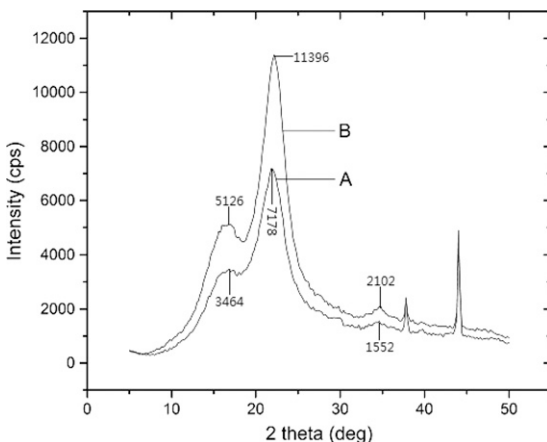


Figure 2. X-ray diffraction curves of natural and modified wood: (A) natural wood, (B) modified wood.

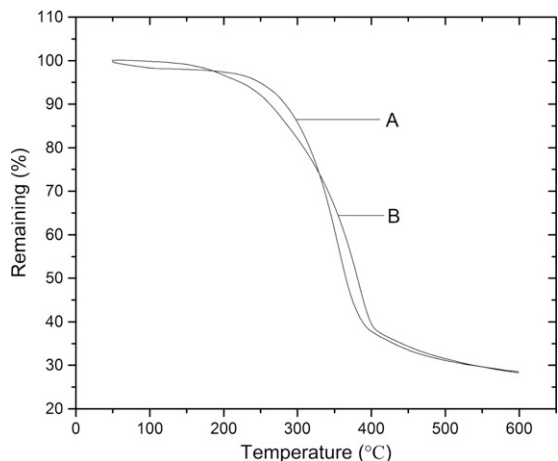


Figure 3. Thermogravimetric analyzer curves of natural and modified wood: (A) natural wood, (B) modified wood.

oxidative decomposition of the remaining lignin. It was evident that the increase in thermo-oxidative stability of modified wood was attributed to the thermal cyclization reaction of prepolymer into the ladder-type thermorigid structure. Overall, natural wood is more stable at temperatures between 170 and 330°C, whereas modified wood is more stable at temperatures between 330 and 410°C. Therefore, the reaction between wood modifier and wood enhanced the stability of cellulose, and the weaker bond reaction was easily broken at high temperature.

Fourier Transform IR Analysis

Figure 4 shows the Fourier transform IR (FTIR) spectra of natural and modified wood. The characteristic peak at 3420 cm^{-1} was assigned to the stretching of hydroxyl groups. Absorbance of hydroxyl groups shifted to lower wavenumber of $3400\text{--}3350\text{ cm}^{-1}$ after modification, which was attributed to the reaction between wood hydroxyl groups and prepolymer. With the decrease of hydroxyl groups, the water uptake and moisture absorption of modified wood decreased. For modified wood, the absorption peak at 1650 cm^{-1} was assigned to amide ($-\text{N}-\text{C}=\text{O}$), which was possibly because of the bond between the function groups ($-\text{NHCH}_2\text{OH}$) of the prepolymer and the wood carbonyl $\text{C}=\text{O}$. Simultaneously, intensity of the absorption band at 1450 cm^{-1} ($-\text{CH}_2-$) decreased after modification, which

can be attributed to the degradation of methylene groups at the end of hemicelluloses and lignin. An increase in the intensity of the absorption peak at 1030 cm^{-1} ($\text{C}-\text{O}$ stretching) evidenced the formation of ether bond, which was caused by the prepolymer impregnation as well (Chang and Chang 2006). Therefore, we inferred that the crosslinking reaction occurred between the prepolymer and wood fiber. Furthermore, the polyacrylic reacted with the hydroxyl groups in the wood, which enhanced the bonding strength between prepolymer and wood.

CONCLUSIONS

The physical and mechanical properties of modified wood, including density, bending strength, MOE in bending, compressive strength parallel to grain, and hardness, were improved. SEM showed that the wood modifier had good dispersion in the cell wall and intercellular spaces. XRD tests indicated that crystallinity of modified wood increased, but the structure of cellulose was not disrupted after modification. TGA analysis showed that the thermal stability of hemicelluloses and cellulose was enhanced after modification. FTIR showed that the hydroxyl groups of wood decreased, which led to the decrease of water absorption of wood. All this proved that the methylolurea and polyacrylic prepolymer was not only impregnated into the wood cell, but also reacted with the wood fiber.

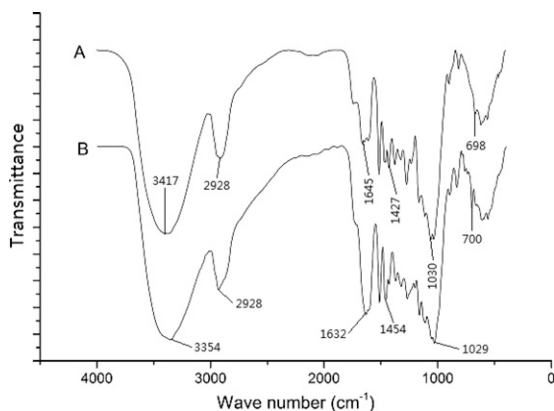


Figure 4. Fourier transform IR curves of natural and modified wood: (A) natural wood, (B) modified wood.

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